

Starch modification techniques and their impact on starch characteristics

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Introduction

Starch is one of the most important food ingredients possessing attributes for innumerable industrial applications. Starch contributes significantly to the texture and sensory properties of processed foods. One-third of total starch produced is utilized for a variety of industrial applications to exploit its unique functional properties such as water absorption, gelation, emulsification, colour formation and structural stability under deformation forces.

Native starches have several technological limitations due to sensitivity towards shear, heat, tendency for retrogradation, not having substantial viscosity, clarity and opacity. Starch modification is an approach followed to overcome these technological challenges and improving the techno-functional properties of starches. The starch modifications methods include physical, chemical and enzymatic treatments. The physical modification methods of starch modification include hydrothermal treatments, such as extrusion cooking (processing and drying), heat-moisture treatment, annealing, radiation, sonication, and pressure treatments. Chemical modification includes substitution, derivatization, etc. While, different enzymes such as amylase, pullulanase could also be employed for enzymatic starch modification.

Physical modification of starch

External physical forces such as heat and shear are applied on native starch to improve its properties. When starch is heat treated under controlled conditions its granular form can be maintained. The functional properties improve upon heat treatment such as improved viscosity, paste clarity and stability upon gelatinization. Physical starch modification can be achieved by heat-moisture treatment (HMT), annealing, extrusion processing, high hydrostatic pressure, pregelatinization of starch etc. Further, in case of HMT and annealing, the granular integrity of starch is maintained and the phenomenon of gelatinization and loss of birefringence are prevented (Stute, 1992). When starch dispersions are heated to severe temperatures with limited amount of water, it is said to be heat-moisture treatment, while in case of annealing, the moisture content is higher to the tune of making starch slurries, but severity of heat treatment is lower than HMT, with below gelatinization temperatures treatment (Collado & Corke, 1999)

Starch source and amylose content affect the degree of changes induced in starch structure and properties upon HMT. The sensitivity of tuber starches is more than legume and cereal starches towards HMT (Hoover & Vasanthan,

1994; Jacobs & Delcour, 1998; Gunaratne & Hoover, 2002). The effect of HMT on various physico-chemical, pasting and thermal properties of different starches has been extensively studied.

Influence of heat-moisture treatment on starch digestibility

It is vital to understand that HMT decreases the digestibility of starch through increasing the resistant starch (RS) content by introducing strong interactions among the molecular starch chains and thereby resulting in compact and rigid configuration inside the starch granules (Chung *et al.*, 2009; Li *et al.*, 2011). RS cannot be digested in the small intestine, but it may be fermented in the large intestine. Corn, pea, and lentil starches when exposed to HMT, showed an increase of 7.7, 11.2 and 10.4%, respectively in the RS content (Chung *et al.*, 2009). Li *et al.*, (2011) reported 2-4 times increment in resistant starch content in *mung* bean starch upon HMT with varying levels of moisture content. On account of crystalline structure formation during HMT, the resistant starch content increases as crystalline form is difficult to digest than amorphous starch. Other possible reasons may be either the interactions between amylopectin and amylose starch chain or because of crystalline polymerization of starch into A+B form resulting from B type. It is assumed that the unit cells of A-type starches are more densely packed than those of B type. The formation of A+B type structure might have increased the proportion of crystalline region and thereby making its enzymatic hydrolysis quite resistant and in turn increasing the resistant starch proportion (Chung *et al.*, 2009; O'Brien & Wang, 2008).

Influence of heat-moisture treatment on starch solubility and swelling power

The solubility of starch depends mainly on the leaching of amylose in the solution. From a starch suspension, when amylose dissociates itself from the starch granules and oozes out from the swollen starch granules, then the starch becomes soluble. This is an indication of increase in degree of disorder from an ordered structure upon heating of starch suspension. Generally, the swelling power decreases with HMT. The amorphous starch fraction is having more affinity towards water and thus in turn is more soluble than the crystalline form. As discussed in the previous section that HMT results in transformation of amorphous form to crystalline, so this explains the lowered swelling capacity of HMT starch than native starch. The phenomenon of reduced solubility has been reported for hydrothermally treated white sorghum and finger millet starch (Olayinka *et al.*, 2008; Adebawale *et al.*, 2005).

Influence of heat-moisture treatment on pasting properties

HMT affects the arrangement of starch chains/molecules thus alter their pasting profile. The peak, breakdown, setback viscosities decrease after HMT while there is increase in pasting temperature (Adebowale *et. al.*, 2005; Olayinka *et. al.*, 2008; Chung *et. al.*, 2009). According to these reports as the moisture level increased during HMT, pasting temperature increased while the peak viscosity decreased in case of white sorghum starch. These two effects of viscosity reduction and pasting temperature increase could be attributed to formation of several cross linkages, resulting in a stronger starch structural integrity, which in turn requires excess heat for disintegrating this structure for even small quantity of water to be absorbed. This is further explained by conversion of amorphous portions into crystalline region through higher number of linkages and thereby inhibiting leaching of amylose molecules in the water phase (Zavareze & Dias, 2011).

Influence of heat-moisture treatment on thermal properties

HMT induces an increase in gelatinization temperatures upon increasing the intensity of treatment through higher moisture and heat application (Zavareze & Dias, 2011). This effect has been observed for various starch types such as corn, finger millet, pea, lentil, tuber crops (Gunaratne & Hoover, 2002; Adebowale *et. al.*, 2005; Adebowale *et. al.*, 2009; Maache-Rezzoug *et. al.*, 2008; Chung *et. al.*, 2009). It has been suggested by Adebowale *et. al.*, (2009) that amylose–lipid and amylose–amylose interactions reduce the mobility of the amorphous region thereby hampering the water penetration inside the starch granules at lower temperature and as a result the increased onset (T_o), peak (T_p), and conclusion (T_c) temperatures for heat-moisture-treated starches.

Chemical modification of starch

Small amounts of approved chemical reagents are used to chemically modify the structure of native starches under defined temperature, pH and other specific reaction conditions. As primarily, the hydroxyl groups are substituted via different chemicals, the functionality of starch changes during chemical modification. Some of the ways of chemical modification include derivatization through the introduction of an ether or ester group in the starch moiety, formation of carbonyl or carboxylic groups through the oxidation of the hydroxyl groups, and also by hydrolysis of glycosidic bonds. There are various factors which affect the functionality and properties of chemically modified starch such as type of starch, reaction conditions, type of derivatization, degree of substitution (DS) and also the way in which the functional group substituted is distribution through the starch moiety (Hirsch & Kokini, 2002).

Octenyl succinic anhydride esterification

Amongst the various types of alkenylsuccinic anhydrides available, octenylsuccinic anhydride (OSA) is currently permitted in many countries for use in food products (Bhosale & Singhal, 2007). Modification using OSA results in amphiphilic behaviour of the modified starch as the hydrophobicity of OSA is introduced in the hydrophilic starch backbone and these types of modified starches are thus suitably used as effective emulsifier. They are also preferred to be used as a controlled release carrier material (Wang *et. al.*, 2011).

The method of preparation of OSA starch by aqueous substitution has been patented by Caldwell & Wurzburg (1953). Later, several workers reported the preparation and characterization of OSA starches. It's a permitted food ingredient in several parts of the world with 3% maximum level of OSA allowed on dry starch weight basis for modification purpose (CFR, 2001). It was long back in 1972, when FDA approved OSA starch for food applications having maximum permitted level of OSA treatment allowed to be 3% and degree of substitution of 0.02.

There are several food products such as sauces, puddings and baby foods, in which OSA starch has been extensively added for different functionalities. One of the major functions for which octenyl succinylated (OS) starch have been widely used is of a fat replacer in emulsified foods (Cho *et. al.*, 1999; Wu *et. al.*, 2006). Some examples include the application of OS corn starch in mayonnaise could successfully replace nearly 82% oil without significantly affecting its rheological characteristics. Also, OS potato starch replaced butter in the ice cream without notably altering the functional and sensory attributed of the product.

Effect of OSA modification on resistant starch

Specific nutritional significance is also associated with OSA starch. OSA starch appeared to be resistant starch as its digestibility is reduced by impairing the binding of α -amylase (Heacock *et. al.*, 2004; Hui *et. al.*, 2009). Further, this less digestibility could be due to the increased stereospecific blockade, which has a shielding effect for starch molecules, caused by introduction of ester groups and long carbon chains to the starch molecules thus being able to retard the enzymatic degradation. These OS groups are primarily positioned on the surface of starch granules and thus reduce the activity of the enzyme hydrolysis (Zhang *et. al.*, 2011).

Effect of OSA modification on pasting properties

The pasting properties of starches are greatly influenced by OSA modification. They have been extensively studied by various workers (Bhosale & Singhal, 2007; Song *et. al.*, 2006; Hui *et. al.*, 2009). According to these reports the incorporation of OSA enhances the overall pasting capacity of the starches. It has been reported that the peak, hot paste, cool paste and breakdown viscosity increases upon OSA

modification while the setback and pasting temperature decreases. The incorporation of a hydrophobic group (OSA) probably facilitates the disruption of highly ordered structure of starch chains thereby allowing more water to penetrate. Therefore, allowing the starch to paste at lower temperature. It has also been suggested in these studies that attached OSA group may disrupt the hydrogen bond of the starch chains and thus makes the starch more readily soluble in water, which leads to formation of further viscous paste than their native counterparts.

Effect of OSA modification on thermal properties

The gelatinization temperature of OS starch depends on the plant origin and degree of substitution. Various workers have reported that the modification of starch using OSA results in decline of gelatinization temperatures (Thirathumthavorn & Charoenrein, 2006; Bhosale & Singhal, 2007; Zhang *et al.*, 2011). The introduction of hydrophobic groups in the starch chain results in weakening of hydrogen bonds and enhanced structural flexibility thereby reducing gelatinization temperature and enthalpy and facilitates starch to swell at lesser temperature (Lawal, 2004).

Effect of OSA modification on rheological properties

The structural strength of starch increases upon OSA modification. The storage (G') and loss (G'') modulus increases after OSA modification. This could be due to the fact that hydrophobic groups attached on the starch chains behave as hydrogen bonding disrupters and in turn increasing the water-solubility of starch moieties, leading to more viscous solutions (Song *et al.*, 2006; Bhosale & Singhal, 2007; Song *et al.*, 2010; Sweedman *et al.*, 2013). Bhandari *et al.*, (2002) reported strong shear thinning behaviour for OSA modified corn and amaranth starch pastes.

Enzymatic modification of starch

The commonly used enzymes for starch modification are amylases. For enzymatic modification of starch, gelatinized dispersion or paste is commonly used owing to increased susceptibility of gelatinized starch to enzyme action. Further, the pH and temperature conditions of enzymes vary with the type and starch source. Apart from α - and β -amylases, pullulanase is also used for starch modification. Pullulanase is a 1,6- α -glucosidase, which acts at linear α -glucan, a pullulan and in turn releases oligomers of maltotriose. In addition to this, it cleaves at α -1,6-glycoside bonds of amylopectin and dextrans having at least two α -1,4-glycoside bonds. Isoamylase; the slow reacting enzyme in comparison to pullulan, which completely hydrolyses α -1,6-glycoside bonds can also be used for enzymatic modification of starch (Kazimierczak *et al.*, 2007). Tapioca and potato starches were enzymatically modified by α -amylase resulting in a starch hydrolysate with dextrose equivalent (DE) value of about 5 or less (Lenchin *et al.*, 1985) at 25–35% solids. Milasinovic *et al.*, (2010) reported that approximately 70% of the normal maize

starch hydrolyzed after 5h using pullulanase enzyme at 2% concentration and it was sufficient for starch debranching.

Conclusion

Starch is an important food constituent determining several product characteristics. At the same time, the application of native starches has posed certain limitations. However, the advancements in technology, particularly starch modification techniques, have helped in great deal by improving starch characteristics such as structural, pasting, thermal properties etc.

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